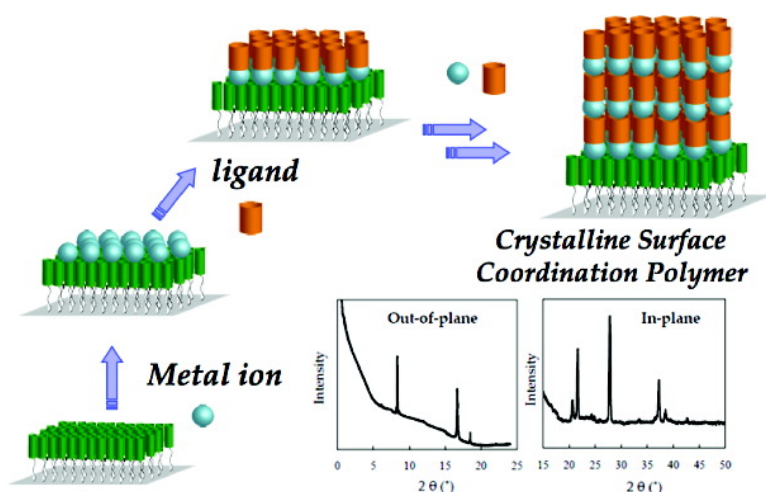


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## Construction of Highly Oriented Crystalline Surface Coordination Polymers Composed of Copper Dithiooxamide Complexes

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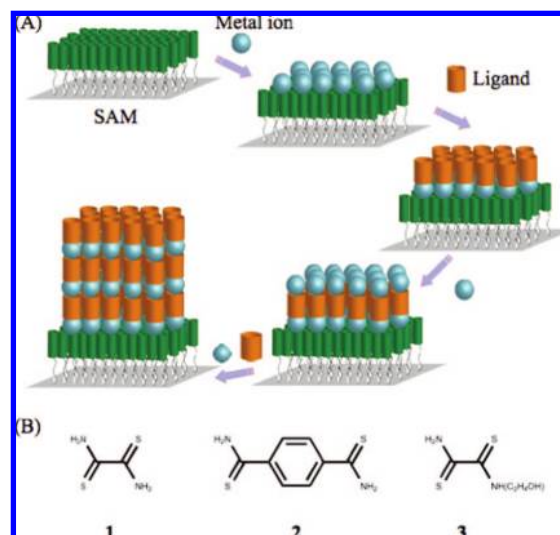
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There are both academic and industrial reasons for fabricating crystals layer by layer on surfaces, and much effort has been devoted to this subject.<sup>1–7</sup> From an academic point of view, there is first evaluation of the techniques and characterization of the quality of the end products. One question that we had asked was “Can we make a crystalline material from components of a material that is amorphous and very difficult to crystallize?” This question originates from our work on copper(II) rubeanate, which is a high-proton conductor that is formed as an amorphous black solid instantly upon reaction of a Cu(II) salt with rubeanic acid.<sup>8,9</sup> This work resulted from recent interest shown in surface metal–organic framework (so-called MOF, CP, or MIL) systems because of their high performance in gas storage, fuel cells, and catalytic activities.<sup>10–12</sup> When considering the transport of protons, electrons/holes, or gases in the framework, crystalline surface metal–organic framework backbones are considered ideal.<sup>13</sup> Two groups have recently reported partially ordered systems by a layer-by-layer fabrication approach.<sup>6,7</sup> However, to the best of our knowledge, highly oriented crystalline surface coordination polymers (SCPs) have not been reported.

Our aim was to organize the inorganic moiety on a surface and then sequentially react it with the organic moiety, followed by the inorganic moiety, to develop the crystal layer by layer (Figure 1A). One difference between our approach and that of Langmuir–Blodgett films is that we do not require molecules with hydrophilic and hydrophobic ends.<sup>14</sup> In our case, each organic ligand and transition metal ion is connected by chemical bonding (Figure 1A). The merits of this bottom-up fabrication technique include precise control of thickness and the arrangement of components of the framework.<sup>15–21</sup> Here, we report a layer-by-layer stepwise fabrication method for the construction of crystalline SCPs and their characterization.

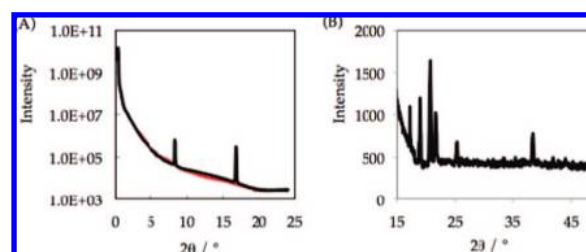
To demonstrate the feasibility of the method, we examined three dithiooxamide compounds (Figure 1B) and two substrates (ultra-smooth sapphire (0001)<sup>22</sup> and glass plates). First, the glass or sapphire substrate was cleaned (see Supporting Information). Then, it was immersed in a 10 mM ethanol solution of aminopropyltrimethoxysilane for 1 h at room temperature to create a binding layer.<sup>23,24</sup> The plate was then washed with ethanol to remove the molecules physically fixed on the substrate and then dried under argon flow. The building blocks of transition metal, copper(II), and organic ligand dithiooxamide were connected on an amino-group-terminated alkyl silane self-assembled monolayer (SAM). The plate with the anchor single layer was then immersed in a 1 mM ethanol solution of dithiooxamide derivative ligand for 15 min at room



**Figure 1.** (A) Conceptual layer-by-layer preparation of crystalline SCP systems. (B) Chemical structures of dithiooxamide ligands.

temperature, washed with ethanol, and then dried. The rubeanic acid terminated film was immersed in a 100 mM copper acetate aqueous solution for 15 min at room temperature, then washed with water, and dried. The latter two processes were repeated for the construction of SCP systems; each repetition of this process is hereafter denoted as a “cycle”.

The reaction between dithiooxamide ligand and copper ion was monitored by QCM (quartz crystal microbalance) measurement. From the decay profile of the frequency of the plate, the reaction time in each process was determined to be 15 min (Figure S1). The processes of layer-by-layer CP formation on glass plates were monitored by UV–vis spectrum measurement. The absorbance of the film increased linearly with the number of immersion steps (Figure S2).



**Figure 2.** (A) Out-of-plane diffraction pattern for a 11 cycle film of Cu-1 (black) and amino-terminated SAM (red) on sapphire. (B) In-plane diffraction pattern of the SCP.

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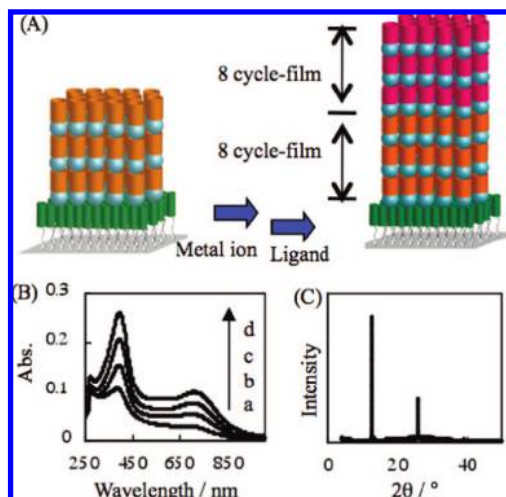
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X-ray diffraction analysis was carried out using synchrotron radiation  $\lambda = 0.10$  nm (SPring-8). Figure 2A shows an out-of-plane XRD of 11 cycle film of Cu-1 on the ultrasmooth sapphire plate compared to the substrate alone. The values of  $2\theta$  of  $8.3^\circ$  and  $16.7^\circ$  indicate that the distance between layers is 0.69 nm. Figure 2B shows the in-plane XRD; six sharp peaks were observed. This means that a periodic structure does exist within the layer that is most likely formed by intermolecular organization through coordination. These sharp peaks have never been observed in the PXRD measurement of bulk CPs. This also indicates that layer-by-layer fabrication on substrates is an excellent technique for obtaining crystalline materials. The evidence of highly oriented SCPs is that both out-of-plane and in-plane XRD patterns were independently obtained. Similar sharp peaks were also obtained in the case of Cu-2 (Figure S3). The values of the thickness, determined using X-ray reflectivity, are 70–100 Å and  $\sim 110$  Å on average for the Cu-1 and Cu-2 layer on the sapphire substrate, respectively.

For comparison, we also measured X-ray scattering/diffraction emanating from Cu-1 and Cu-2 grown on a glass substrate. The ultrasmooth sapphire substrate was specially prepared and had a periodically repeated surface structure composed of an atomically flat terrace and step. On the other hand, the glass substrate had an isotropic surface structure without such an atomic-scale structure. Not many peaks were recorded in the profiles in Figure S4 compared with the numbers of peaks shown in Figure 2. The peak at  $33.65^\circ$  in Figure S4 did not appear in Figure 2B taken for the in-plane geometry; however, the peak at  $16.7^\circ$  appeared in both Figure S4 for the in-plane geometry and Figure 2A for the out-of-plane geometry. This implies that the atomically flat terrace prefers an orientation of the adsorbed molecules. The terrace may play the role of controlling the atomic configuration. Interestingly, no peaks were observed in the in-plane diffraction profile when the asymmetric ligand **3** was employed (Figure S5). This means that the reaction between the dithioamide ligand and copper(II) ion cannot be controlled at substrate surfaces. The symmetry of the molecules is an important factor for obtaining the crystalline SCPs. The AFM images of SCPs indicate that the size of the domain of  $\pi$ -extended Cu-2 is larger than the normal Cu-1 (Figure S8), probably because of the  $\pi$ - $\pi$  interaction between phenyl groups of the molecules.



**Figure 3.** (A) Conceptual view of homostructured crystal and heterostructured crystals. (B) UV-vis absorption spectra of (a) 2, (b) 4, (c) 6, and (d) 8 cycle film of Cu-1 on the 8 cycle film of Cu-2 on glass plate. (C) Out-of-plane XRD for 8 cycle film of Cu-1 on 8 cycle film of Cu-2 on glass plate.

Having established the formation of crystals with Cu-1 and Cu-2, we attempted the fabrication of heterocrystals of copper dithioamide derivatives. Figure 3A shows UV-vis spectra of two, four, six, and eight cycle films of Cu-1 on the eight cycle film of Cu-2. The new absorption band of the SCP was observed, and it increased with the number of dipping cycles. Figure 3B shows the X-ray powder diffraction pattern of the eight cycle film of Cu-1 plus an eight cycle film of Cu-2 (measured on a laboratory diffractometer,  $\lambda = 0.154$  nm). The observation of sharp peaks indicates that heterocrystal SCPs are feasible. It should be noted that the sharp diffraction peaks were obtained not only on sapphire but also on glass substrates.

In summary, we have for the first time successfully constructed crystals of SCPs layer by layer from the corresponding components from materials with amorphous bulk states. This method can be useful for fabricating Josephson junctions of superconductors, magnetic spin valves, capacitance, screen displays, fuel cells, and catalytic devices.

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**Supporting Information Available:** Materials, QCM, XRD, XPS, and AFM images of the SCPs are shown. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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